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Layering and mixing in coadsorbed xenon-ethylene films on graphite

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X-ray and neutron diffraction are used to probe the structures of coadsorbed xenon and ethylene films on graphite. Both layering and mixing transitions are observed. Little or no ethylene is found to wet a xenon-covered graphite surface at low temperature.

Despite the importance of wetting in many biological and surface chemical processes, the conditions which cause one material to spread over the surface of another are not, as yet, well understood in microscopic terms. Thermodynamic arguments[1] suggest that three different growth modes are possible when a clean substrate is exposed to an adsorbate. Discrete layers may form on the substrate no matter how thick the film, a process known as complete wetting. Alternatively, only a limited number of layers may form with additional material appearing as a coexisting bulk phase. This is known as partial wetting. Finally, there is the possibility of nonwetting. In this case, no layering occurs at all, and only the bulk adsorbate phase appears.

Sullivan[2] and, later, Pandit, Schick, and Wortis[3] have proposed that these differences in wetting behavior originate from an underlying competition between the microscopic forces of cohesion and adhesion. In terms of the relative strengths of the adhesive (adsorbate-substrate) and cohesive (adsorbate-adsorbate) interactions u and v, respectively, they suggested that complete wetting occurs when $u/v \gg 1$, partial wetting when $u/v \sim 1$, and nonwetting when $u/v \ll 1$.

Relatively few experimental surveys of wetting and layering have been made to date. The most complete —those on gold[4] and graphite[5-9] substrates—show that although complete wetting is common in liquid films, partial wetting is much more likely when solid films form. And even in those few instances where complete solid-on-solid wetting was observed, there was no obvious correlation with large values of u/v.

In attempting to look more directly at the influence of adhesive and cohesive interactions on wetting and layering processes, we took a typical partial wetting system, ethylene on graphite, and modified the substrate by introducing a second, strongly adhering absorbate—xenon. Ethylene, we found, does not wet a xenon-covered graphite surface at low temperatures. Nevertheless, layering transitions remarkably like those in the pure system take place at higher temperatures, and, as we will show, when they occur they are accompanied by the formation of two-dimensional ethylene-xenon solid solutions.

To explore fully the properties of two-component overlayers requires that the behavior of each component be investigated separately. This we were able to do by combining the results of x-ray and neutron-diffraction measurements, since x rays are strongly scattered by xenon but not by ethylene, while for neutrons exactly the opposite situation prevails. Our x-ray measurements were made on C_2H_4 with a rotating-anode source using 1.54-Å Cu $K\alpha$ radiation. For the neutron measurements (made on C_2D_4) a triple-axis spectrometer operated in the elastic mode with neutrons of either 2.38 or 4.04 Å wavelength was employed. Collimations were such that the instrumental wave-vector resolution, half width at half maximum (HWHM), was approximately 0.01 Å^{-1} for the x rays; for the neutrons the HWHM was about 0.013 Å^{-1} at the shorter wavelength and 0.017 Å^{-1} when the longer wavelength was used. In both sets of measurements the substrate consisted of a lightly compressed, exfoliated graphite powder, the neutron sample being somewhat more compressed than the x-ray sample because the greater surface area per unit volume gave higher intensity. The surface area of the x-ray sample was determined from a krypton adsorption isotherm measurement; for the neutron sample, a nitrogen isotherm was used. Coverage is thus defined on a scale in which unit coverage represents a $\sqrt{3}\times\sqrt{3}$ registered monolayer. We note, however, that neither xenon nor ethylene forms such an exactly commensurate solid overlayer, although both come near to registry. Three representative mixtures of xenon and ethylene were investigated: one with a xenon-to-ethylene ratio of 0.2:0.8 (total coverage: one registered monolayer), a second with a ratio of 1:1 (total coverage: two registered monolayers), and a third with a ratio of 1:6 (total coverage: seven registered monolayers). In both the x-ray and neutron measurements, the diffraction pattern of the overlayer film was obtained by subtracting the empty-cell scattering. The x-ray measurements were also corrected for absorption. Whether xenon was preadsorbed at a higher temperature than ethylene or both gases were mixed and then adsorbed, the resultant diffraction profiles were the same.

Before discussing the two-component film data, it will be helpful to review briefly some of the relevant properties of xenon and ethylene monolayer films adsorbed on graphite basal plane surfaces. Submonolayer xenon forms an incommensurate, triangular-lattice solid with a nearest-neighbor (NN) distance between 4.56 and 4.32 Å depending on coverage and temperature. Correspondingly, the lowest-index Bragg reflection from the film—the (10) reflection that will be of interest here—appears at values of the wave vector Q between 1.59 and 1.68 Å^{-1}. Melting occurs at ~100 K at all coverages between 0.1 and 0.73 monolayers; above 0.73 monolayers the melting temperature rises, reaching 146 K at unit coverage, and continues to higher temperatures as the coverage is further increased. Near unit coverage and for temperatures below ~65 K, xenon is thought to undergo a phase transition to a stripe-domain structure[6] with $Q_{10}=1.695$ Å^{-1}. Xenon on graphite is one of the few known solid-on-solid systems that wets to a depth of at least six layers at low temperature.

Adsorbed ethylene[7] has a more complicated low-temperature phase diagram. At coverages below 0.83 monolayers, it forms a low-density, incommensurate, triangular-lattice solid, called the LD solid, with a NN distance of 4.65 Å ($Q_{10}=1.56$ Å^{-1}). Above this coverage there is a two-phase region where the LD solid and a second, denser solid, labeled the HD solid, coexist. Increasing the coverage to 1.04 monolayers transforms the film completely into the HD phase. Like the LD solid, the HD solid has an incommensurate, triangular-lattice structure, but the NN distance is reduced to 4.22 Å ($Q_{10}=1.72$ Å^{-1}). Configuration energy calculations and steric considerations suggest that the C—C axes of the molecules are parallel to the film plane in the LD phase and shift to a perpendicular orientation at the higher HD phase density. Melting of the LD phase takes place at 68 K. When the HD solid is heated, however, it undergoes a structural phase transition at 72 K, reverting before melting, to an incommensurate, triangular-lattice solid with a NN distance of 4.42 Å ($Q_{10}=1.64$ Å^{-1}). It is important to note that this high-temperature phase, labeled the compressed-LD solid in Ref. 8, is essentially identical in structure to the solid xenon monolayer. As the coverage is increased above 0.83 monolayers (the LD phase boundary), the melting temperature of the monolayer rises, finally stabilizing at 90 K at coverages of 1.04 monolayers and above. Ethylene-on-graphite is a partial wetting system. In the most recent studies,[8] layering transitions were identified at 75, 98, and 101 K. Only the 75-K transition is a solid-on-solid transition, however.

Turning now to our x-ray and neutron-diffraction investigations of the xenon-ethylene (0.2:0.8) monolayer, diffraction profiles like those in the left half of Fig. 1 were observed at all temperatures below 65 K. In the x-ray scan there is a strong, asymmetric, two-dimensional (2D) powder pattern peak at $Q=1.65$ Å^{-1}—identifiable as the (10) peak of the triangular-lattice solid xenon submonolayer—and a weaker, but recognizable, ethylene contribution at 1.73 Å^{-1}. The neutrons, on the other hand, show only a well-defined ethylene peak at $Q=1.72$ Å^{-1}, the characteristic (10) peak of the HD ethylene 2D solid phase. (The ethylene peak is shifted to a slightly larger value of Q in the x-ray scan because the coverage was evidently a little higher and the film therefore somewhat more compressed.) Above 69 K, as is evident in the right half of Fig. 1, both x-ray and neutron scans show similar peaks at 1.61 Å^{-1}, indicating a transition in the ethylene film and the formation of an incommensurate 2D solid phase in which ethylene and xenon are indistinguishable. Two other observations that were made should also be mentioned: First, the ethylene structural transition (presumably the HD-to-compressed-LD phase transformation) shifts monotonically to lower temperatures with increasing xenon concentration and, second, the high-temperature solid phase that forms above the transition melts at a temperature some 6–10 K higher than that of the equivalent compressed LD phase in the pure ethylene system. What all this information suggests is that the monolayer separates at low temperatures into either pure xenon and ethylene phases or, more likely, into xenon-rich and ethylene-rich phases, and that at a higher temperature a mixing transition converts the overlayer into a 2D xenon-ethylene solid solution with almost the same structure as the equivalent pure xenon and compressed LD solid ethylene phases. This mixing transition possibly coincides with the ethylene HD-to-compressed-LD phase transition at 65–69 K.

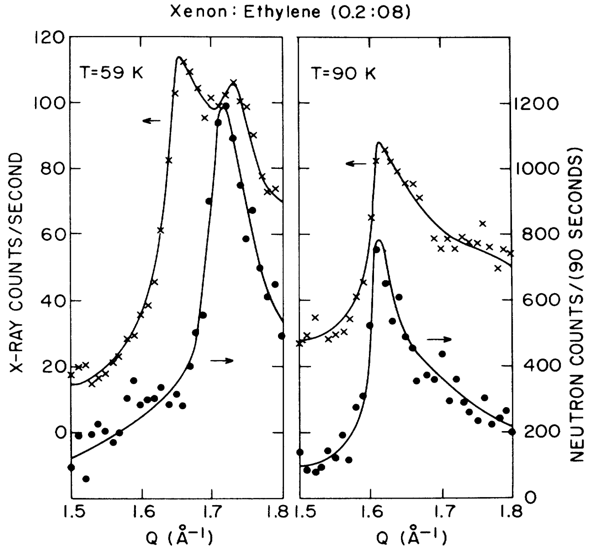

FIG. 1. (10) x-ray (upper) and neutron (lower) diffraction peaks from a xenon: ethylene 0.2:0.8 monolayer. The asymmetric profiles identify the scattering as arising from disordered arrays of two-dimensional crystallites. The solid lines are guides to the eye.

Looking now at the xenon:ethylene 1:1 diffraction data, we note that the 40-K profiles, plotted in the left half of Fig. 2, show a typical asymmetric, two-dimensional x-ray

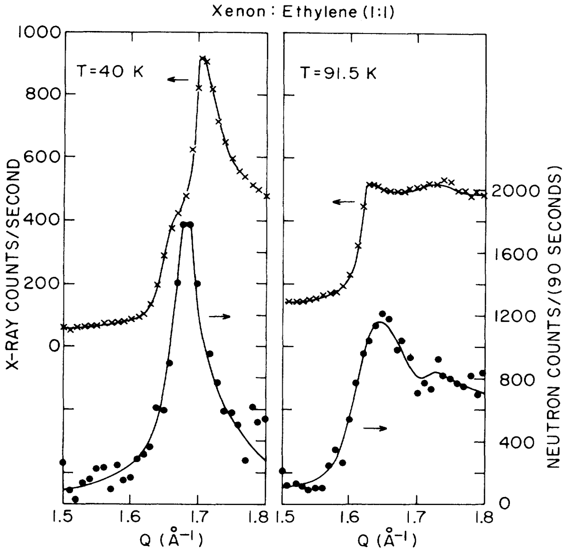

FIG. 2. (10) x-ray and neutron diffraction peaks from a xenon: ethylene 1:1 bilayer. The more flattened profiles at the right identify them as originating from two-dimensional solid bilayers. The symmetric neutron profile at the left identifies it as three dimensional in origin. The solid lines are guides to the eye.

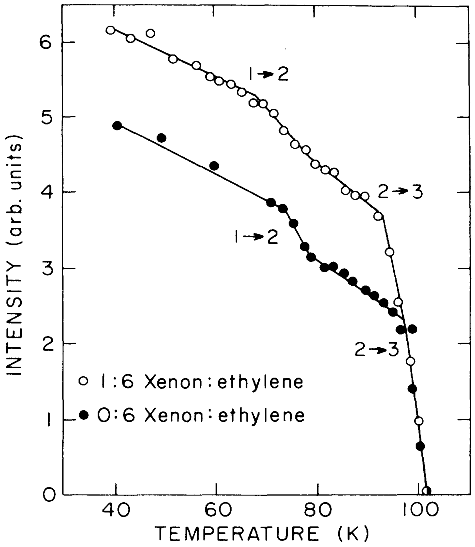

FIG. 3. Temperature dependence of the diffracted neutron intensity measured from the (200) peak of the bulk monoclinic solid ethylene phase. Layering transitions appear as sharp changes in slope. The solid lines are guides to the eye.

monolayer xenon peak at ~1.70 Å^{-1}, with structure on its leading edge which is identifiable, in the neutron scan, as a symmetric, three-dimensional ethylene diffraction peak. This (110) peak and others seen in the neutron data are indexed by the known monoclinic structure of bulk ethylene. At this higher coverage the ethylene appears to have been driven off the surface; it now forms a three-dimensional bulk phase which coexists with a compressed pure xenon (or at least xenon-rich) monolayer film which is very nearly commensurate.

From the 91.5-K x-ray and neutron scans, plotted in the right half of the figure, it is clear that striking changes take place in the 1:1 film at higher temperatures. Both peaks are now markedly asymmetric, nearly identical, and have become noticeably flatter than the monolayer profiles of Fig. 1. These flattened profiles—the identifying feature of diffraction from two-dimensional, structurally ordered bilayers[8]—first appear at 82 K when second-layer formation (which begins at 68 K) is nearly complete and persist to about 95 K. Since x rays and neutrons see the same line shape, both xenon and ethylene must be present in each layer, and we infer that layering and mixing transitions have taken place (possibly at the same time) and the coexisting 3D and 2D phases have been replaced by a xenon-ethylene solid-solution bilayer which melts at a higher temperature (95 K) than the pure ethylene bilayer (90 K) but not as high as its pure xenon equivalent (> 155 K). At the onset of melting, the leading edge of the bilayer profile is observed to broaden, and as the ethylene coverage is increased above one monolayer a new peak appears at 1.73 Å^{-1}. This structure is as yet unexplained, but its occurrence seems to coincide with the next layering transition and the corresponding addition of ethylene to the surface. It is probably the origin of the slight bump at 1.73 Å^{-1} in the high-temperature profiles.

To look in detail at subsequent layering transitions we turn to our xenon:ethylene 1:6 data. At temperatures below 68 K we see, as in the 1:1 film, a pure xenon (or xenon-rich) monolayer coexisting with bulk, monoclinic solid ethylene. In such a system, layering transitions can be easily identified by monitoring the intensities of the bulk ethylene diffraction peaks. Figure 3 shows the temperature dependence of the ethylene diffracted intensity as observed with neutrons. Data for pure ethylene-on-graphite are also included for comparison. In the xenon-ethylene and pure ethylene films the onset of second-layer formation appears as a change in slope at 68 and 74 K, respectively. At 104 K (the triple point of monoclinic solid ethylene) the bulk ethylene phase melts and complete wetting begins in both systems. Note that although the layering transitions in the pure film appear to take place at slightly higher temperatures than in the two-component film there is otherwise little difference in their wetting behavior. Also note that the ratio of intensities in Fig. 3 is consistent with this interpretation.

To summarize, xenon, which is roughly twice as strongly bound to graphite as ethylene,[9] drives it off graphite surfaces at low temperatures, the displaced gas forming a bulk solid phase. However, layering at higher temperatures is little affected by the presence of the xenon. The 74-K, one-to-two solid-layer transition in the pure ethylene-on-graphite system, for example, is replaced in the xenon: ethylene (1:6) system by a transition at 68 K in which a solid xenon monolayer is converted to a mixed xenon-ethylene solid bilayer. A temperature difference of only four degrees separates the next, two-to-three liquid layer transition in the two systems. The complete wetting transition at 104 K is unaltered. Remarkably, drastic modification of layer composition and (presumably) surface adhesion seem not to disturb the basic pattern of the layering process significantly.

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[1] J. G. Dash, Phys. Rev. B **15**, 3136 (1977).

[2] D. E. Sullivan, Phys. Rev. B **20**, 3991 (1979).

[3] R. Pandit, M. Schick, and M. Wortis, Phys. Rev. B **26**, 5112 (1982).

[4] J. Krim, J. G. Dash, and J. Suzanne, Phys. Rev. Lett. **52**, 640 (1984).

[5] J. L. Seguin, J. Suzanne, M. Bienfait, J. G. Dash, and J. A. Venables, Phys. Rev. Lett. **51**, 122 (1983).

[6] H. Hong, M. Sutton, and R. J. Birgeneau (unpublished).

[7] S. K. Satija, L. Passell, J. Eckert, W. Ellenson, and H. Patterson, Phys. Rev. Lett. **51**, 411 (1983).

[8] M. Sutton, S. G. J. Mochrie, and R. J. Birgeneau, Phys. Rev. Lett. **51**, 407 (1983); S. G. J. Mochrie, M. Sutton, R. J. Birgeneau, D. E. Moncton, and P. M. Horn, Phys. Rev. B **30**, 263 (1984).

[9] M. Bienfait, J. L. Seguin, J. Suzanne, E. Lerner, J. Krim, and J. G. Dash, Phys. Rev. B **29**, 983 (1984).